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ALEX PUNNOOSE AND CHARLES HANNA

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Geosciences
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14. ABSTRACT
This project was based on the PI's research during 2005-2010 as part of a NSF-CAREER award, on the ferromagnetic properties of pure and transition metal doped oxide semiconductors such as SnO2, ZnO, and CeO2, reported in 40 refereed research papers. In this ARO project, studies on ultra small particles of these oxides with crystallite sizes of 2-5nm have shown room temperature ferromagnetism in undoped samples. Interestingly, in oxide nanoparticles doped with transition metal ions such as Fe and Co, the magnetic moment per dopant ion

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Report Title

SEMICONDUCTOR-BASED NANOTECHNOLOGY APPLICATIONS : FINAL REPORT

ABSTRACT

This project was based on the PI's research during 2005-2010 as part of a NSF-CAREER award, on the ferromagnetic properties of pure and transition metal doped oxide semiconductors such as SnO2, ZnO, and CeO2, reported in 40 refereed research papers. In this ARO project, studies on ultra small particles of these oxides with crystallite sizes of 2-5nm have shown room temperature ferromagnetism in undoped samples. Interestingly, in oxide nanoparticles doped with transition metal ions such as Fe and Co, the magnetic moment per dopant ion decreased with increasing their concentration, thus suggesting that the magnetic properties are not arising from the dopant ions. The observed magnetic moment in these materials scales with oxygen defect concentration determined from catalytic studies, thus indicating the major role of oxygen defects in the magnetic properties of nanoscale oxide semiconductors. Magnetic Properties of Fe doped, Co Doped and Fe+Co co-doped ZnO nanoparticles showed that charge transfer between co-doped metal ions contributes to ferromagnetism. Thin film structures using Co doped SnO2 were fabricated and studied their usefulness in device applications. NP of semiconducting oxides such as ZnO were also used to investigate their cytotoxicity and preferential cancer cell killing in several types of human cells.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. A simple route to A simple aqueous solution route to ultrasmall SnO2 nanoparticles, Gordon Alanko and Alex Punnoose, Poster presentation at the Materials Science and Technology conference, Pittsburgh, October 2011.

2. J. Beltran, J. Osorio, C. Barrero and A. Punnoose, Magnetic Properties of Fe doped, Co Doped and Fe+Co co-doped ZnO Accepted for presentation in the 57th Magnetism and Magnetic Materials conference (AIP), Chicago, January 2012,

3. Zebrafish xenograft model of glioblastoma to investigate structure activity relationships of zinc oxide nanoparticles with anticancer properties, Leah C. Wehmas, Lisa Truong, Jeffrey A. Greenwood, Alex Punnoose, & Robert L. Tanguay, First Sustainable Nanotechnology Organization Conference, November 4-6, 2012 at the Hilton Arlington, VA
4. Selective toxicity of zinc oxide nanoparticles to cancer cells, Invited talk, Alex Punnoose, Department of Biophysics and Biochemistry, Oregon State University, May 9, 2012.
5. Size, Surface Structure and Doping Effects on Ferromagnetism in SnO2. Gordon Alanko**, Aaron Thurber, Charles Hanna and Alex Punnoose. 56th Magnetism and Magnetic Materials conference (AIP), October 30–November 3, 2011, Scottsdale, Arizona.
6. Highly shape-selective synthesis, silica coating, self-assembly, and magnetic stability of hematite nanoparticles. Jianhui Zhang, Aaron Thurber, Charles Hanna and Alex Punnoose. 56th Magnetism and Magnetic Materials conference (AIP), October 30–November 3, 2011, Scottsdale, Arizona.
7. Ferromagnetic properties of Fe doped CeO2 nanoparticles. G. L. Beausoleil**, G. Alanko**, Charles Hanna, S. Srinivasa Rao and Alex Punnoose, 56th Magnetism and Magnetic Materials conference (AIP), October 30–November 3, 2011, Scottsdale, Arizona
8. Unusual crystallite expansion and modification of ferromagnetism due to aging in pure and doped ZnO nanoparticles. Aaron P. Thurber, Kelsey N. Dodge**, Gordon Alanko**, Geoffrey L. Beausoleil II**, Charles Hanna and Alex Punnoose. 56th Magnetism and Magnetic Materials conference (AIP), October 30–November 3, 2011, Scottsdale, Arizona.
9. Synthesis and Characterization of Transition Metal-doped ZnO; Lytia A. Smith**, Theron R. Fereday**, Jerry D. Harris, Jason Brotherton**, Aaron Thurber, William B. Knowlton, Alex Punnoose and Brian J. Frost, poster presentation at the Spring 2010 National Meeting of the American Chemical Society (San Francisco, California, March 21 - 25, 2010).
10. Magnetism of ZnO Nanoparticles: Dependence on crystallite size and surfactant coating ,Aaron P. Thurber, Geoffrey L. Beausoleil II**, Gordon A. Alanko**, Joshua J. Anghel**, Michael S. Jones**, Lydia M. Johnson*, Jianhui Zhang, C. B. Hanna, D. A. Tenne, and Alex Punnoose, 55th Magnetism and Magnetic Materials conference (AIP) in Atlanta, November 2010.
11. An EPR study of CeO2 nanoparticles: Effect of doping with 5% Co or Ni ions and varying annealing temperature, S. K. Misra, S. I. Andronenko, J. D.Harris, A. Thurber, G. L. Beausoleil II** and A. Punnoose, 55th Magnetism and Magnetic Materials conference (AIP) in Atlanta, November 2010.
12. Synthesis and Characterization of ZnO Sol-gel Powders; Amanda R. Snyder**, Lytia A. Smith**, Theron R. Fereday**, Jerry D. Harris, Aaron Thurber, Jason Brotherton, Pamela Walker, William B. Knowlton, and Alex Punnoose, poster presentation at the Spring 2010 National Meeting of the American Chemical Society (San Francisco, California, March 21 - 25, 2010).
13. Growth and Characterization of ZnO Thin Films; Theron Fereday**, Lytia Smith**, Amanda Snyder**, Jerry D. Harris, Aaron Thurber, Jason Brotherton**, William B. Knowlton, Alex Punnoose, Seth M. Hubbard, and Brian J. Frost, poster presentation at the Spring 2010 National Meeting of the American Chemical Society (San Francisco, California, March 21 - 25, 2010).

Number of Presentations: 13.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

? Alex Punnoose was awarded the Boise State University Distinguished Professorship, most prestegious honor that can be accorded to a faculty member to recognize excellence in teaching, research and public service (one of the seven Boise State University Distinguished Professors selected from 535 faculty members, by a university-wide committee, see http://news.boisestate.edu/update/2011/04/30/boise-state-names-six-faculty-as-inaugural-%E2%80%98distinguished-professors%E2%80%99/)

? Alex Punnoose received the 2012 Jean'ne Shreeve Research Excellence Award from Idaho NSF-EPSCoR, established to recognize the accomplishments of a faculty member at Boise State University, Idaho State University, the University of Idaho or other state institution of higher education who has previously been an active participant in the NSF EPSCoR program.

? Alex Punnoose was a Finalist of the 2010 Idaho Innovation Award in the Early-Stage innovation category organized by the Idaho Technology council in 2010 for the research discovery (U.S. Patent No. 8,187,638) titled "Novel Nanoparticles That Kill Cancer Cells" (http://news.boisestate.edu/update/2010/10/28/researchers-honored-at-2010-idaho-innovation-awards/)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Lydia Johnson	1.00	
Jailes Beltran	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Srinivasa Rao Singamaneni	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Alex Punnoose	1.00	No
Charles Hanna	1.00	
Denise Wingett	1.00	
Dmitri Tenne	1.00	
FTE Equivalent:	**4.00**	
Total Number:	**4**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Caitlin Otto	0.25	Biosciences
Chad Van Komen	0.48	Physics
Geoffrey Beausoleil	0.48	Physics
Jordan Chess	1.00	Physics
Lucy McCall	0.25	Physics
Gordon Alanko	0.50	Physics
Michael Jones	0.50	Physics
Kelsey Dodge	1.00	Biosciences
Jonas Abdo	0.50	Physics
Maryan Sabetian	0.50	Biosciences
Joshua Anghel	0.48	Physics
Andrew Farrar	0.48	Physics
FTE Equivalent:	**6.42**	
Total Number:	**12**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	7.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	5.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	5.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	4.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	2.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	5.00

Names of Personnel receiving masters degrees

NAME
Lydia Johnson
Total Number: **1**

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Aaron Thurber	1.00
Jailes Beltran	1.00
FTE Equivalent:	**2.00**
Total Number:	**2**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Our recent experiments on pure and transition metal doped oxide semiconductors such as SnO_2, ZnO and CeO_2 clearly demonstrated that room-temperature ferromagnetism can be produced in these systems. There is a strong rle for the transition metal dopants, but their magnetic moment is not directly contributing to the magnetism or exchange interaction. Magnetism in these materials are related to oxygen vacancies and defects. Efforts are on to increase and control defects and the room temperature ferromagnetism. Ferromagnetism in these oxide nanoparticles depends strongly on their surface structure. Modifying the surface structure of oxide nanoparticles, we have recently shown that both magnetic and photoluminescence properties can be tailored.

ZnO nanoparticles display strong cytotoxicity to certain bacterial systems and human cells. Our combined experimental and theoretical modeling studies demonstrated that electrostatic interactions between the charged ZnO nanoparticles and the bacterial cells play a major role in the cytotoxic response. In human cells, however, both electrostatics and reactive oxygen species play major roles in the observed cytotoxicity.

A new method to detect hydrogen gas by monitoring the changes in the magnetic properties of hematite nanoparticles has been developed.

When prepared in nanoscale size range, most semiconductor oxides including ZnO, SnO_2 and TiO_2 show strong photocatalysis due to their large surface to volume ratio and the presence of oxygen vacancies and defects. When these nanoparticles are doped with transition metals, the electron-hole recombination rate can be controlled well and also their photocatalytic activity.

Technology Transfer

PUBLICATIONS RESULTED FROM THE ARO GRANT

1. Role of oxygen defects on the magnetic properties of ultra-small Sn1-xFexO2 nanoparticles, K. Dodge**, J. Chess**, G.Alanko**, C. Hanna and A. Punnoose, Accepted for presentation in the Magnetism and Magnetic Materials conference, January 12-15, 2013, Chicago and submitted for publications in *Journal of Applied Physics* (2013).

2. Correlation between magnetism and electronic structure of $Zn_{1-x}Co_xO$ nanoparticles, Chess, Jordan; Alanko, Gordon; Farrar, Andrew K.; Tenne, Dmitri A.; Hanna, Charles B; Punnoose, Alex, Accepted for presentation in the Magnetism and Magnetic Materials conference, January 12-15, 2013, Chicago and submitted for publications in *Journal of Applied Physics* (2013).
3. Magnetic Properties of Fe doped, Co doped and Fe+Co co-doped ZnO, J.J. Beltran, J. A. Osorio, C. A. Barrero, C. B. Hanna and A. Punnoose" Accepted for presentation in the Magnetism and Magnetic Materials conference, January 12-15, 2013, Chicago and submitted for publications in *Journal of Applied Physics* (2013).

4. Oscillatory magnetism and photoluminescence in metal oxide nanocrystals capped with surfactant, Jianhui zhang, SJ Xiong, XL Wu, Aaron Thurber, Michael Jones, Ming Gu, Dmitri Tenne, Charles Hanna, and Alex Punnoose, submitted to Nature Publishing Group Asia Materials (2012).

5. Tuning the magnetism and photoluminescence of ZnO, TiO_2, SnO_2, and CeO_2 nanospheres by modifying the capping surfactant, Jianhui Zhang*, Aaron Thurber, Michael Jones, Min Gu, Xinglong Wu, Dmitri A. Tenne, C. B. Hanna, and Alex Punnoose, Advanced Materials (Accepted 2012).

6. Size, Surface Structure and Doping Effects on Ferromagnetism in SnO_2. Gordon Alanko**, Aaron Thurber, Charles Hanna and Alex Punnoose. Journal of Appled Physics, J. Appl. Phys. **111**, 07C321 (2012).

7. Concentration dependence of magnetic moment in $Ce_{1-x}Fe_xO_2$, G. L. Beausoleil**, G. Alanko**, Charles Hanna, S. Srinivasa Rao and Alex Punnoose, Journal of Appled Physics, **111**, 07B546 (2012).

8. Unusual crystallite expansion and modification of ferromagnetism due to aging in pure and doped ZnO nanoparticles. Aaron P. Thurber, Kelsey N. Dodge**, Gordon Alanko**, Geoffrey L. Beausoleil II**, Charles Hanna and Alex Punnoose. Journal of Appled Physics, **111**, 07C319 (2012).

9. Improving the selective cancer killing ability of ZnO nanoparticles using Fe doping, Aaron Thurber, Denise G. Wingett, John W. Rasmussen, Janet Layne*, Lydia Johnson*, Dmitri A. Tenne, Jianhui Zhang, Charles B. Hanna, and Alex Punnoose, Nanotoxicology, June 2012, Vol. 6, No. 4 : Pages 440-452.

10. Tuning the properties of ZnO, hematite, and Ag nanoparticles by adjusting the surface charge, Jianhui Zhang, Guanjun Dong, Aaron Thurber, Yayi Hou*, Min Gu, Dmitri A. Tenne, C. B. Hanna, and Alex Punnoose, Advanced Materials 24:1232-7 (2012).

11. Synthesis and Characterization of chromium-isothiocyanate-4-methylpyridine complexes, J. L. Young**, J. D. Harris, J. A. Benjamin**, J. E. Fitch**, D. F. Nogales**, J. R. Walker, B. J. Frost**, A. Thurber and A. Punnoose, Inorganica Chimica Acta, 377, 14-19 (2011).

12. A Large Scale Synthesis and Characterization of Quaternary $CuIn_xGa_{1-x}S_2$ Chalcopyrite Nanoparticles via Microwave Batch Reactions," by Chivin Sun, Richard Westover, Gary Long, Cyril Bajracharya*, Jerry Harris, Alex Punnoose, Rene G. Rodriguez and Joshua J. Pak, International Journal of Chemical Engineering, Volume 2011, Article ID 545234, 8 pages (2011).

13. Magnetism of ZnO Nanoparticles: Dependence on crystallite size and surfactant coating ,Aaron P. Thurber, Geoffrey L. Beausoleil II**, Gordon A. Alanko**, Joshua J. Anghel**, Michael S. Jones**, Lydia M. Johnson*, Jianhui Zhang, C. B. Hanna, D. A. Tenne, and Alex Punnoose, *Journal of Applied Physics*, 109, 07C305 (2011).

14. Enhanced Dye Fluorescence in novel Dye-ZnO nano-composites. Jianhui Zhang, Aaron Thurber, Dmitri Tenne, Denise Wingett, Charles Hanna, and Alex Punnoose, *Advanced Functional Materials* 20, 4358 (2010).

15. Transition metal dopants essential for producing ferromagnetism in metal oxide nanoparticles, Lydia Johnson, Aaron Thurber, Josh Anghel**, Maryam Sabetian**, Mark H. Engelhard, D. Tenne, Charles Hanna and Alex Punnoose, Physical Review B 82, 054419 (2010).

16. Highly shape-selective synthesis, silica coating, self-assembly, and magnetic hydrogen sensing of hematite nanoparticles, Jianhui Zhang, Aaron Thurber, Charles Hanna and Alex Punnoose, *Langmuir 26*, 5273 (2010).

17. Correlation between saturation magnetization, bandgap and lattice volume of transition metal (M = Cr, Mn, Fe, Co or Ni) doped $Zn_{1-x}M_xO$ nanoparticles; J. Anghel**, A. Thurber, D. Tenne, C. B. Hanna, A. Punnoose, *Journal of Applied Physics* 107, 09E314 (2010).

18. Electrostatic interactions affect nanoparticle-mediated toxicity to the Gram-negative bacterium *Pseudomonas aeruginosa* PAO1. Kevin Feris, Caitlin Otto**, Juliette Tinker, Denise Wingett, Alex Punnoose, Aaron Thurber, Madhu Kongara, Maryam Sabetian**, Bonnie Quinn, Charles Hanna, David Pink, *Langmuir*, **2010**, *26* (6), pp 4429–4436.